

## ***E. Mathematical Equations for Fate and Transport Evaluation***

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### **E.1 Drainage Area Proration Factors**

Because flow rate data from the USGS gages at Coltsville and Great Barrington have indicated an approximately uniform runoff rate within the watershed (i.e., Section 2.4.1), drainage area proration provides a sufficiently accurate method for estimating the average flow rate at particular locations along the Housatonic River. This approach is based on the following equation:

$$Q_{loc} = (DA_{loc} / DA_{colt}) Q_{colt} \quad (E.1-1)$$

where:  $Q_{loc}$  = estimated tributary flow rate (cfs);  
 $Q_{colt}$  = Coltsville flow rate (average of 105 cfs);  
 $DA_{loc}$  = tributary drainage area (mi<sup>2</sup>); and  
 $DA_{colt}$  = Coltsville drainage area (57.6 mi<sup>2</sup>).

Note that the drainage area ratio (i.e.,  $DA_{loc} / DA_{colt}$ ) is referred to as the Drainage Area Proration (DAP) factor. These factors and estimated average flow rates at various locations within the system are listed in Table E.1-1.

**Table E.1-1. Estimated average flow rates at various locations and tributaries.**

<b>Location or Tributary</b>	<b>Drainage Area (mi<sup>2</sup>)</b>	<b>DAP Factor</b>	<b>Mean Flow Rate (cfs)</b>
West Branch	60	1.03	108
East Branch at Dawes/Pomeroy Avenue	69	1.19	125
Holmes Road Bridge	128	2.22	233
Sackett Brook	11	0.19	20
Roaring Brook	8	0.14	14
New Lenox Road Bridge	143	2.48	260
Yokun Brook	6	0.10	11
Woods Pond Dam	168	2.91	306
Schweitzer Bridge	169	2.93	308

## E.2 Suspended Sediment Rating Curves

Measured TSS concentration data can be used to estimate tributary and in-river solids loading rates through application of sediment rating curves, which have the following form:

$$C_{ss} = C_{low}, \quad Q \leq Q_{mean}$$

$$C_{ss} = C_{high} (Q/Q_{mean})^n, \quad Q > Q_{mean} \quad (E.2-1)$$

where:

$C_{ss}$	=	suspended sediment concentration (mg/L);
$Q$	=	local flow rate (cfs);
$Q_{mean}$	=	local mean flow rate (cfs);
$C_{low}$	=	low-flow constant;
$C_{high}$	=	high-flow constant; and
$n$	=	site-specific exponent.

A commonly-used correction coefficient (Ferguson 1986) is used to account for the bias that results from the transforming of rating curves from logarithmic space into normal space. The correction coefficient, which is a function of the variance of the log-transformed TSS concentrations, is lumped into  $C_{high}$  for simplicity in Equation (E.2-1). This equation was applied to the Housatonic River data by using flow rates measured at the USGS Coltsville gaging station and drainage area proration (see Appendix E.1) to estimate flow rates at several other locations. This approximation introduces uncertainty into the sediment rating curves for these locations; however, this approach is still useful for providing estimates of sediment loads on an annual timescale. The corresponding rating curve parameter values are listed in Table E.2-1. Note that the break point in the sediment rating curve between low- and high-flow conditions is at the mean flow rate.

**Table E.2-1. TSS rating curve parameters for eight locations within Reaches 5 and 6.**

Location	$C_{low}$	$C_{high}$	$n$	$Q_{mean}$ (cfs)
East Branch, Hubbard Avenue	2.6	2.6	1.00	105
Dawes/Pomeroy Avenue Bridge	3.6	5.6	1.08	125
West Branch	3.5	5.1	0.99	108
Holmes Road Bridge	4.3	9.0	0.63	233
Sackett Brook	1.2	2.8	1.34	20
New Lenox Road Bridge	4.0	6.3	0.96	260
Woods Pond Headwaters	3.7	3.2	1.02	306
Woods Pond Dam	5.4	4.5	0.34	306

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### E.3 Equilibrium Partitioning Coefficients

Generally, the sorptive tendency of PCBs is described by an organic carbon-referenced sorption partition coefficient ( $K_{oc}$ ;  $L^3/M$ ) that describes the equilibrium ratio of sorbed chemical concentration to dissolved chemical concentration after the sorption reaction has attained equilibrium:

$$K_{oc} = \frac{c_s / f_{oc}}{c_d} \quad (E.3-1)$$

where:  $c_d$  = freely dissolved water column PCB concentration ( $M L^{-3}$ );  
 $c_s$  = sorbed PCB concentration ( $M M^{-1}$ ); and  
 $f_{oc}$  = organic carbon fraction of the solids.

$K_{oc}$  is typically treated as a basic property of an organic chemical that is independent of the sorbent material.  $K_{oc}$  is proportional to other properties of the chemical that are related to hydrophobicity, such as the octanol/water partition coefficient ( $K_{ow}$ ).

PCBs are known to partition to dissolved and colloidal organic matter in both the water column and sediment. The partition coefficient describing the equilibrium sorption of PCBs to dissolved/colloidal organic matter is typically expressed on an organic carbon basis and is termed  $K_{doc}$ :

$$K_{doc} = \frac{c_{doc} / m_{doc}}{c_d} \quad (E.3-2)$$

where:  $c_{doc}$  = PCB concentration sorbed to DOC ( $M L^{-3}$ ); and  
 $m_{doc}$  = DOC concentration ( $M L^{-3}$ ).

The value of  $K_{doc}$  is typically less than that of  $K_{oc}$ . For example, Evans (1988) found that  $K_{doc}$  values for three PCB congeners sorbing to natural dissolved/colloidal organic matter from ten lakes and two streams in south-central Ontario were 0.2 to 4% of the corresponding  $K_{ow}$  values.

If equations E.3-1 and E.3-2 are combined to express the three phase  $K_{oc}$  as a function of measured parameters, the following expression is obtained:

$$K_{oc} = \frac{c_s}{f_{oc} c_d'} (1 + m_{doc} K_{doc}) \quad (E.3-3)$$

where:  $c_d'$  = the effective total PCB concentration measured in the pore water (i.e., freely dissolved plus DOC-sorbed phases;  $M L^{-3}$ ).

This equation can be solved for paired sediment-pore water samples if the reasonable assumption that  $K_{doc}$  is 10% of  $K_{ow}$  is made (e.g., Poerschmann and Kopinke 2001). For the purposes of the sediment calculations in the Report,  $K_{ow}$  was calculated based on published congener specific values (Hawker and Connell 1988) and the PCB congener composition of the samples. For surface water data, it was assumed that  $K_{doc}$  is 1% of  $K_{ow}$  (compared to 10% used in the calculation of sediment/pore water partition coefficients). This difference was

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used to represent the difference in the nature of the carbon between the water column and sediments (i.e., the DOC data suggest a low level of refractory carbon present in the water column, as opposed to larger organic molecules that are produced during decomposition of detritus in the bed and are would therefore be in a more labile form).

## E.4 Diffusion Flux of PCB from Surface Sediments to the Overlying Water Column

The diffusive flux of PCB from sediment pore water to the water column can be described by the following mass flux equation:

$$J_s = k_f A_s (c_d' - c_{d,wc}) \quad (\text{E.4-1})$$

where:

$J_s$	=	diffusive mass loading (M/T);
$k_f$	=	the sediment/water mass transfer coefficient (L/T);
$A_s$	=	sediment surface area (L <sup>2</sup> );
$c_d'$	=	the effective total PCB concentration measured in the pore water (i.e., freely dissolved plus DOC-sorbed phases; M L <sup>-3</sup> ); and
$c_{d,wc}$	=	water column PCB concentration (M/L <sup>3</sup> ).

For hydrophobic compounds such as PCB,  $c_d'$  is much greater than  $c_{d,wc}$ . Therefore  $c_{d,wc}$  can be removed from the above equation. Using 3-phase equilibrium partitioning coefficients to express pore water concentration ( $c_d'$ ) as a function of sediment PCB concentration ( $c_s$ ), organic carbon fraction ( $f_{oc}$ ), and DOC concentration ( $m_{doc}$ ), the sediment diffusive flux equation becomes:

$$J_s = k_f A_s \frac{c_s}{f_{oc} K_{oc}} (1 + m_{doc} K_{doc}) \quad (\text{E.4-2})$$

This equation provides a means of estimating diffusive PCB loading from Housatonic River sediments using surficial sediment PCB and TOC concentrations. For the calculations in this Report, the river was divided into one-mile sections between the Confluence and Woods Pond Headwaters. For each section, the average sediment organic carbon-normalized PCB concentration was calculated using 1998-2002 surface sediment (0-6") data (e.g., Figure 4-13). Organic carbon normalized PCB concentration is the ( $c_s / f_{oc}$ ) term in Equation (E.4-2). Table E.4-1 summarizes the values used for the remaining parameters in the diffusive flux equation.

**Table E.4-1. Parameters used in the low flow sediment PCB diffusive flux calculation.**

Parameter		Value	Units	Source
$k_f$	sediment/water exchange	0.003	m/d	estimated
$A_s$	sediment surface area	calculated	m <sup>2</sup>	GIS analysis for each section
$m_{doc}$	pore water DOC concentration	16.5	mg/L	2001 EPA/GE data (see Section 8.4)
$K_{oc}$	OC partition coefficient	$2.5 \times 10^6$	L/kg	2001 EPA/GE data (see Section 8.8.1.2)
$K_{doc}$	DOC partition coefficient	$2.5 \times 10^5$	L/kg	estimated 10% of $K_{oc}$ (Appendix E.3)

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## E.5 Volatilization Flux Analysis

The importance of volatilization within the main channel areas of the River was evaluated using an upper bound calculation for Woods Pond. In this analysis, a steady-state mass balance calculation is used to estimate the loss of water column PCBs via volatilization under low-flow conditions:

$$V \frac{dc}{dt} = Qc_{in} - Qc - J_v A_s \quad (= 0 \text{ for steady state}) \quad (\text{E.5-1})$$

where:

$V$	=	volume of pond ( $\text{L}^3$ );
$Q$	=	flow rate ( $\text{L}^3 \text{T}^{-1}$ );
$c_{in}$	=	water column PCB concentration entering pond ( $\text{M L}^{-3}$ );
$c$	=	water column total PCB concentration within pond ( $\text{M L}^{-3}$ );
$J_v$	=	volatilization flux ( $\text{M L}^{-2} \text{T}^{-1}$ ); and
$A_s$	=	surface area of pond ( $\text{L}^2$ ).

The rate at which volatilization occurs is dependent on the mass transfer coefficient at the air-water interface and the concentration of PCBs in the water column. Only freely-dissolved PCB can be transported across the interface, so sorption to particulate or dissolved organic carbon reduces volatilization. The PCB flux from the water column due to volatilization is expressed as follows:

$$J_v = k_L \left( c_d - \frac{c_{air}}{H} \right) \quad (\text{E.5-2})$$

where:

$k_L$	=	volatilization mass transfer coefficient ( $\text{L T}^{-1}$ );
$c_d$	=	freely dissolved PCB concentration in water ( $\text{M L}^{-3}$ );
$c_{air}$	=	vapor phase PCB concentration in air ( $\text{M L}^{-3}$ ); and
$H$	=	dimensionless Henry's Constant.

This steady-state mass balance for Woods Pond can be simplified by combining equations E.5-1 and E.5-2, setting  $c_{air}$  equal to zero (based on air monitoring PCB data from the Woods Pond region discussed in Section 7), and expressing  $c_d$  as the product of the fraction dissolved ( $f_d$ ; from equilibrium partitioning) and the total water column PCB concentration:

$$\frac{c}{c_{in}} = \frac{1}{1 + \frac{A_s k_L f_d}{Q}} \quad (\text{E.5-3})$$

The volatilization mass transfer coefficient is dependent on the rates of mass transfer through relatively thin layers of water and air at the interface, which are in turn dependent on the concentration gradients in the layers, and the diffusivity of PCBs in the layers (O'Connor 1983, 1984):

$$k_L = \frac{k_g k_l}{k_g + \frac{k_l}{H}} \quad (\text{E.5-4})$$

where:  $k_g$  = vapor phase mass transfer constant ( $\text{L T}^{-1}$ ); and  
 $k_l$  = water phase mass transfer constant ( $\text{L T}^{-1}$ ).

A Henry's Law Constant of  $5 \text{ Pa}\cdot\text{m}^3/\text{mol}$ , which corresponds to a dimensionless value (i.e.,  $H$  in E.5-2) of 0.0021 at  $20^\circ\text{C}$ , was used in this calculation. This value was estimated based on published Henry's Law Constants for PCB congeners (Brunner et al. 1990) in the penta to hexa range, which is consistent with the mean composition from dissolved water column data from Woods Pond (Section 3.8). The liquid phase mass transfer coefficient ( $k_l$  in Equation E.5-4) was calculated from the O'Connor-Dobbins equation (O'Connor and Dobbins 1958):

$$k_l = \sqrt{\frac{D_w U}{h}} \quad (\text{E.5-5})$$

where:  $D_w$  = molecular diffusivity (defined below) of PCBs in water ( $\text{L}^2 \text{T}^{-1}$ );  
 $h$  = mean water depth (L); and  
 $U$  = average current velocity ( $\text{L T}^{-1}$ ).

This equation predicts that mass transfer is positively related to current velocity, which reflects the fact that increased turbulence tends to increase the effective surface area of the air-water interface, and thereby the efficiency of gas-liquid exchange. Molecular diffusivity for this expression was calculated using the equation presented by Hayduk and Laudie (1974):

$$D_w = \frac{13.26 \times 10^{-5}}{\mu^{1.14} (\bar{V})^{0.589}} \quad (\text{E.5-6})$$

where:  $\mu$  = water viscosity (centipoise); and  
 $\bar{V}$  = PCB molar volume ( $\text{cm}^3/\text{mol}$ ).

The molar volume was assigned a mean value of  $300 \text{ cm}^3/\text{mol}$  based on the average homolog composition observed in the Woods Pond water column data (Section 3.8) and published homolog-specific molar volumes for PCBs (Mackay et al. 1992a). Using this value results in a molecular diffusivity of  $4.6\text{E-}6 \text{ cm}^2/\text{s}$ . The average depth in Woods Pond was estimated to be 1.5 m based on bathymetry data (Section 2.2.2.2; Figure 2-9). Based on 1999-2001 EPA measurements, a representative current velocity measured at Woods Pond Footbridge under low flow (corresponding to a flow of approximately 50 cfs at Coltsville) of 0.05 m/s was used for this calculation.

Using the values described above in equation E.5-5 yields an estimate for  $k_l$  of 0.34 m/d. The vapor phase mass transfer coefficient ( $k_g$  in Equation E.5-4) was assumed to be a constant value of 100 m/d, which is a reasonable approximation for streams and rivers (O'Connor 1983). Based on these values and the estimated Henry's Constant, equation E.5-4 evaluates to an overall volatilization mass transfer coefficient of 0.13 m/d. Substituting this coefficient, a typical low flow at Woods Pond of 100 cfs (Section 2.4), a dissolved PCB

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fraction of 0.4 (Section 8.8.1.2), and the total surface area of Woods Pond of 270,000 m<sup>2</sup> into equation E.5-3 yields an estimate of  $(c / c_{in})$  equal to 0.95. This calculation suggests that volatilization would cause water column dissolved PCB concentrations to decrease across Woods Pond by approximately 5% under typical low-flow conditions.



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## E.6 Bank Erosion Sediment Load Estimate

An order-of-magnitude estimate of the annual sediment mass load to the River from bank erosion, can be made using the following equation:

$$M_{bank} = \rho_b L_b h_b E_b \quad (E.6-1)$$

where:

$M_{bank}$	=	bank erosion mass loading ( $M T^{-1}$ );
$\rho_b$	=	bank dry density ( $M L^{-3}$ );
$L_b$	=	total length of eroding bank (L);
$h_b$	=	average bank height (L); and
$E_b$	=	annual average bank erosion rate ( $L T^{-1}$ ).

Approximate values for the reach of the river where EPA mapping identified areas of active bank erosion are:  $\rho_b = 1.5 \text{ g/cm}^3$ ,  $L_b = 13,400 \text{ ft}$ , and  $h_b = 8 \text{ ft}$ . It was assumed in this analysis that the average bank erosion rate ranges from 0.3 to 0.7 ft/yr, based on the averages from EPA toe pin data and bank measurements between the Confluence and New Lenox Road Bridge. The result was an estimated range of 1400 to 3200 metric tons/yr of sediment load to the river from bank erosion.

## E.7 Resuspension Potential

A field study was conducted by GE during June 1997 to measure the resuspension properties of cohesive sediments in the Housatonic River. A portable resuspension device, commonly referred to as a shaker, was used to measure the erosion properties of surficial sediment cores collected from the Woods Pond, Columbia Mill, Willow Mill, Glendale, Rising Pond, Falls Village and Bulls Bridge Dam impoundments. A total of 42 surficial cores were obtained from these seven backwaters and typical shaker procedures were used to test the cores (Ziegler 1998). The objective of the field study was to obtain site-specific parameters for the Lick equation:

$$\varepsilon = A(\tau / \tau_{cr} - 1)^n \quad (\text{E.7-1})$$

where:  $\varepsilon$  = sediment resuspension potential (mg/cm<sup>2</sup>);  
 $\tau$  = bottom shear stress (dynes/cm<sup>2</sup>);  
 $\tau_{cr}$  = critical shear stress (=1 dyne/cm<sup>2</sup>);  
 $A$  = site-specific parameter; and  
 $n$  = site-specific parameter.

Measured values of  $\varepsilon$  from this study for applied shear stresses of 3, 5, and 9 dynes/cm<sup>2</sup> are listed in Table E.7-1.

**Table E.7-1. Housatonic River resuspension potential data.**

Dam Backwater	Core	$\varepsilon_3$	$\varepsilon_5$	$\varepsilon_9$
Woods Pond	1	1.4	8.4	11
Woods Pond	2	3.7	14	18
Woods Pond	3	1.1	6.3	10
Woods Pond	4	4.7	11	21
Woods Pond	5	10	14	109
Woods Pond	6	5.8	21	68
Woods Pond	7	8.2	29	103
Woods Pond	8	0.8	5.0	28
Woods Pond	9	7.8	24	109
Columbia Mill	1	0.8	1.0	16
Columbia Mill	2	2.1	9.4	41
Columbia Mill	3	0.0	1.4	14
Columbia Mill	4	0.7	2.1	9.2
Willow Mill	1	0.1	1.8	43
Willow Mill	2	0.4	1.1	14
Willow Mill	3	0.2	2.0	26
Willow Mill	4	0.5	0.7	3.3
Willow Mill	5	0.6	2.6	12
Glendale	1	2.3	9.1	53
Glendale	2	1.6	3.8	26
Glendale	3	0.9	2.8	18
Glendale	4	1.6	7.7	37
Glendale	5	1.4	5.8	53
Glendale	6	4.1	22	132
Rising Pond	1	0.8	2.1	11
Rising Pond	2	1.2	5.6	44

Dam Backwater	Core	$\epsilon_3$	$\epsilon_5$	$\epsilon_9$
Rising Pond	3	2.1	5.9	7.0
Rising Pond	4	0.2	1.2	9.5
Rising Pond	5	0.0	0.4	5.8
Rising Pond	6	3.9	18	132
Falls Village	1	0.9	4.8	40
Falls Village	2	0.4	2.3	23
Falls Village	3	0.9	4.8	35
Falls Village	4	0.6	1.8	39
Falls Village	5	3.0	8.7	59
Falls Village	6	1.0	5.1	29
Falls Village	7	1.4	3.5	17
Bulls Bridge	1	2.1	7.9	35
Bulls Bridge	2	1.3	4.9	43
Bulls Bridge	3	2.2	8.0	48
Bulls Bridge	4	1.2	3.9	29
Bulls Bridge	5	2.7	9.1	111

Regression analyses based on a linearization of Equation E.7-1 were used to estimate values of  $A$  and  $n$  for each core. Values of the exponent ( $n$ ) ranged from 1.5 to 3.3 for the seven impoundments; this range of exponent values is similar to that found in other river systems (e.g., Lick et al. 1995). The constant,  $A$ , in the Lick equation ranged over approximately two orders of magnitude (i.e., 0.016 to 1.5 mg/cm<sup>2</sup>), with this amount of variation in cohesive sediment erosion properties being typical.

The resuspension data for Woods Pond were used to estimate the relative erodibility of cohesive sediments in this riverine system. Similar shaker studies have been conducted in the Upper Hudson River, NY (Ziegler et al. 2000); Lower Fox River, WI; Saginaw River, MI; and Buffalo River, NY (Lick et al. 1995). Scour depths were estimated using  $A$  and  $n$  values for Woods Pond and the other four rivers, where the current velocity and bed dry density were assumed be 2 ft/s and 0.4 g/cm<sup>3</sup>, respectively. The resulting scour depths for Woods Pond, the Upper Hudson River, Lower Fox River, Saginaw River, and Buffalo River are: 2.0, 1.8, 8.0, 1.6 and 0.8 mm, respectively. Thus, the erodibility of Woods Pond cohesive sediments is similar to that found in other rivers.

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## E.8 REFERENCES

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